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Comparative study of the application of radial and axial passive sampling strategies to the determination of volatile organic compounds in air

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BACHELOR'S THESIS

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Agraïments

Vull expressar el meu agraïment a tots aquells que m'han acompanyat en aquest viatge i han posat el seu granet de sorra perquè aquest treball de fi de grau arribés a ser el que és ara. El suport i l'ajuda que he rebut durant aquest procés han estat immesurables i essencials pel seu èxit.

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Abstract

Volatile organic compounds (VOCs) are considered essential parameters for the assessment of air quality, due to their effects on both the environment and human health. Different strategies are in use for their determination, of which passive samplers are especially interesting due to the easy operability of the commercially available options, but their uptake rates seem to be affected by factors other than the nature of the sampler and of the analyte. This work compares the results obtained by analysis with two types of passive samplers (axial and radial) followed by TD-GC-MS with those obtained by an online GC-PID-based analyser, during periods of time with varying environmental conditions. Out of all the studied compounds, benzene and the three isomers of xylene are the only ones for which there is agreement between online GC and passive sampling in these specific conditions.

Sinopsi

Els compostos orgànics volàtils (COVs) són considerats paràmetres essencials per l’avaluació de la qualitat de l’aire, a causa dels seus efectes en el medi ambient i en la salut humana. Actualment s’empren diferents estratègies per la seva determinació, entre els quals destaquen els mostrejadors passius per la fàcil operació de les opcions comercialment disponibles, però sembla que les seves constants de difusió es veuen afectades per factors aliens a la natura del mostrejador i de l’anàlit. Aquest treball compara els resultats obtinguts per l’anàlisi amb dos tipus de mostrejadors passius (axials i radials) seguits de TD-GC-MS amb aquells obtinguts per un analitzador en línia basat en GC-PID, durant períodes de temps amb condicions ambientals variables. De tots els compostos estudiats, el benzè i els tres isòmers de xilè són els únics pels quals hi ha concordança entre el GC en línia i el mostreig passiu en aquestes condicions específiques.

Acronyms and abbreviations

BTEX: Benzene, toluene, ethylbenzene and xylenes (*ortho*-, *meta*- and *para*-)

CI: Chemical ionisation

EI: Electron ionisation

GC: Gas chromatography

LOD: Limit of detection of the instrument

LOQ: Limit of quantification of the instrument

MDL: Method detection limit

MQL: Method quantification limit

MS: Mass spectroscopy

TD: Thermal desorption

VOCs: Volatile organic compounds

1. Introduction

Volatile organic compounds (VOCs) are considered essential parameters for the assessment of air quality, due to their effects on both the environment and human health. For this reason, they have attracted the attention of and been thoroughly studied by environmental science.

VOCs are defined by the Industrial Emissions Directive of the European Union[1] as "any organic compound […] having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use". This definition encompasses a wide variety of compounds, so a more detailed recalling of their effects and abundance in the study area is required to select those which will be included in this work.

The most relevant effect of VOCs on the environment is their involvement in photochemical smog and their role as ozone precursors. Photochemical smog arises from the reactions between nitrogen oxides (NO and NO_2) and VOCs in the presence of sunlight, and their main products are ozone (O_3) and other oxidant compounds. The accumulation of these products in the troposphere, the layer of the atmosphere closest to the surface of the Earth, can have harmful oxidizing effects on not only humans and human-made materials but also animals and plants[2].

Although the European Union recommends monitoring of all those VOCs which are classified as ozone precursors[3], only the ambient concentration of benzene is regulated to an annual average of 5 $\mu g \cdot m^{-3}$ in immision zones. 1,3-butadiene is regulated in other regions of the world, such as in Ontario, Canada[4] with a maximum annual average of 2 $\mu g \cdot m^{-3}$ and in the United Kingdom[5] with a maximum annual average of 2.25 $\mu g \cdot m^{-3}$.

Regarding human health, the effects caused by their continued inhalation can be classified as either non-carcinogenic or carcinogenic. Non-carcinogenic effects caused by long-term exposure are acute respiratory damage, increasing the risk of asthma, and damage to the nervous, immune, and reproductive systems. VOCs have also been related to symptoms such as fatigue, headaches, dizziness, nausea, lethargy, and depression[2].

Benzene, trichloroethylene, and 1,3-butadiene are classified by the International Agency for Research on Cancer (IARC)[6] as Group 1 agents, which means they are carcinogenic to humans. In fact, benzene has been proved to have sufficient evidence as an agent related to different types of leukaemia, with limited evidence of its relation to lung cancer, non-Hodgkin lymphoma and multiple myeloma. There is also sufficient evidence of the relations between trichloroethylene and kidney cancer and between 1,3-butadiene and leukaemia, lymphoma and multiple myeloma[7]. Other studied VOCs with carcinogenic activity classified by IARC are styrene, tetrachloroethylene and 1,1,1-trichloroethane as Group 2A agents (probably carcinogenic) and 1,4-dichlorobenzene and ethylbenzene as Group 2B agents (possibly carcinogenic). The rest of the studied VOCs are not classifiable as to their carcinogenicity to humans.

The area of Tarragona hosts one of the largest chemical and petrochemical complexes of Europe. Its industrial production is divided in two main zones, Tarragona's North Park and Tarragona's South Park, which between them host 34 different companies[8]. Some of the selected VOCs are part of their products, such as benzene and 1,3-butadiene, and others are raw or process materials they use.

Both the effects of VOCs on the environment and on human health, as well as their presence and manipulation in the study area which can lead to the existence of peaks in their concentration, accentuate the need for reliable and simple methods for their monitoring and determination. This work consists of the application of different strategies to their analysis in the field, with the aim to compare their performance and reliability.

Goals

The main goals of this project are:

- To determine the concentrations of various volatile organic compounds (VOCs) in ambient air samples from urban areas close to petrochemical industrial parks.
- To validate a method for axial and radial passive sampling of VOCs in ambient air using thermal desorption coupled to GC-MS.
- To compare the performance of axial and radial passive samplers for the determination of VOCs, both between them and with the results obtained with an online analyser.
- Check the effect of meteorological conditions on the uptake rates of passive samplers.

Objectius

Els objectius principals d'aquest projecte són:

- Determinar les concentracions de diversos compostos orgànics volàtils (COVs) en mostres d'aire ambient d'àrees urbanes pròximes polígons industrials petroquímiques.
- Validar un mètode per mostreig passiu axial i radial de COVs en aire ambient emprant desorció tèrmica acoblada a GC-MS.
- Comparar el funcionament de mostrejadors passius axials i radials per la determinació de COVs, entre ells i amb els resultats obtinguts amb un analitzador en línia.
- Comprovar l'efecte de les condicions meteorològiques sobre les constants de difusió dels mostrejadors passius.

2. Theoretical background

2.1. Sampling of VOCs

Both active and passive sampling strategies are currently in use for the analysis of VOCs in air and are considered suitable for their determination at low concentrations levels, since they include a preconcentration step which increases sensitivity when compared to whole-air sampling methods using bags or canisters. Out of the two, passive samplers are especially interesting due to the large number of commercially available options with different structures (badges, radial tubes, axial tubes) and their easy operability.

These samplers rely on diffusion of the analytes from air to an adsorbent. This phenomenon is described by Fick's first law, from which the following expression[9] (*Equation 1*) is derived,

$$\frac{dm}{dt} = D \cdot \frac{A}{L} \cdot (C_o - C_a) \tag{1}$$

where m is the mass of adsorbed analyte (µg), t is the sampling time (min), D is the diffusion coefficient of the analyte in air (m^2 min^{-1}), A is the area of the sampler (m^2), L is the length of the gaseous layer (m), C_o is the concentration of the analyte in air (µg m^{-3}), and C_a is the concentration of analyte in the layer directly adjacent to the surface (µg m^{-3}). This expression can be simplified by assuming that analytes are adsorbed immediately, making the last concentration equal to zero, and by simplifying the term $D \cdot A/L$ as the uptake rate (U), which depends on the sampler's geometry and will therefore remain constant for different analysis with the same type of sampler. By applying these boundary conditions and simplifications, *Equation 2* is obtained.

$$C_o = \frac{m}{t \cdot U} \tag{2}$$

Since this expression depends on the uptake rate and that depends on the geometry (*Figure 1*) of the sampler, the different existing sampler structures show different performances. Axial tubes, with a small diffusion surface and a long diffusion path, usually have low uptake rates, while radial tubes, with a large diffusion surface, tend to have the highest uptake rates out of the three types. The performance of badges tends to lie somewhere in the middle.

The main problem with passive sampling is that these uptake rates seem to be affected by many factors other than the nature of the sampler and of the analyte, such as the presence of other heavier VOCs which can compete for the adsorption[10]. And especially for radial passive samplers, several previous studies[11–13] have shown that their uptake rates are somewhat variable due to changes in sampling time, temperature, wind velocity, ambient air concentration, and humidity.

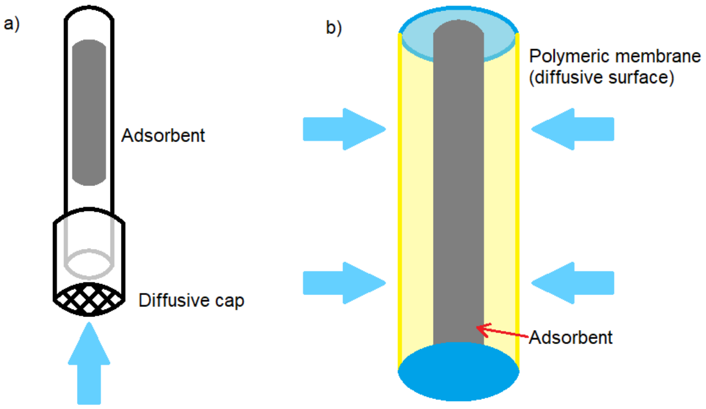


Figure 1. a) Axial passive sampling tube with diffusive cap and showing the direction in which air enters the sampler. b) Radial passive sampling tube with diffusive surface and showing the direction in which air enters the sampler.

Strandberg et al.[11] calculated the uptake rates for benzene and 1,3-butadiene using Radiello® diffusive samplers filled with Carbopack X sorbent and saw that these rates remain more or less constant for benzene but suffer a significant decrease for the analysis of 1,3-butadiene with the prolongation of the sampling period (24h to 1 week). High air humidity (>65%) also has a great effect, decreasing the uptake rates by about 30%. Other studies[10] even saw some decreases with time in the uptake rates of light VOCs such as benzene and toluene.

The most plausible explanation for the dependence of uptake rates on the length of the sampling period would be reverse diffusion[11,12,14] of the target compounds, especially 1,3-butadiene. This phenomenon occurs when the concentration differential becomes negative, meaning that the concentration of the compound on the surface of the adsorbing material is much larger than its ambient concentration. In that case, part of the analytes retained on the sorbent could be lost through back diffusion to air.

Therefore, as seen by Urpina et al.[13], the use of radial samplers for the determination of 1,3-butadiene could be unreliable when there are great variations of ambient concentration during the sampling period. The real values are greatly underestimated when samplers are exposed to a high concentration of the target compound followed by a long period of low concentration, since part of the analyte is lost through reverse diffusion. On the other hand, concentrations are greatly overestimated when the peak of concentration occurs at the end of the sampling period. And these changes caused by reverse diffusion seem to be increased by temperature as well.

The small diffusion surface of axial tubes, though, makes them resistant to these changes in environmental conditions, and it seems that reverse diffusion is not as significant in that case. Both types of passive sampling have been compared with active sampling in the mentioned studies, but that has only been done for few compounds (1,3-butadiene, benzene, toluene, and *m*-xylene) and mostly in controlled laboratory conditions.

This study is based on a comparison between the two types of passive samplers when used in the field. This means that the environmental conditions (temperature, wind velocity and direction, humidity) uncontrollably change both during each sampling period and between them. The presence of an industrial site, where the analytes are used and produced, close to the sampling point means that their concentrations in ambient air will also be irregular, which as seen before could lead to misestimation of the real values when using radial samplers. Thus, discrepancy between the results obtained with the two types of passive samplers is expected, especially for 1,3-butadiene.

2.2. TD-GC-MS

The radial and axial tubes used as passive samplers are analysed by thermal desorption coupled to gas chromatography and mass spectrometry (TD-GC-MS).

Thermal desorption is based on the heating of the analytes retained on a solid adsorbent so that they are volatilized and extracted by the flow of an inert gas. It has many advantages when compared to other types of extraction, since no solvent is required, and it can easily be coupled to gas chromatography for automation. These characteristics increase the sensitivity and lower the limits of detection, because no further sample manipulation is needed and that significantly decreases the accumulation of errors and the loss of analytes.

The desorption process consists of two stages (*Figure 2*), the tube desorption and the trap desorption. In the first stage, the sorbent tube is heated and the compounds are desorbed and dragged away by the carrier gas into a focusing cold trap, where they are condensed due to the low temperatures obtained by cryogenisation with a nitrogen flow. The cold trap contains a sorbent (or a mixture of sorbents) which retains the analytes until the second stage starts. In this stage, the trap is rapidly heated and a small flux of carrier gas drags the concentrated analytes to the chromatographic column, where they are separated. The trap desorption step includes a split so that a higher flux of carrier gas can pass through the trap to clean it and increase its lifespan without entering the column and endangering it with an overflow.

Gas chromatography is highly efficient for the separation of VOCs. The most common columns used for this purpose are capillary apolar columns with a silicon based stationary phase, such as (5% phenyl-95% dimethylpolysiloxane), because they offer a good separation and can be used for a wide range of compounds[15], but mid-polar columns containing cyanopropyl and phenyl groups are also manufactured specifically for separation of VOCs. The column used in this work will be of the first kind.

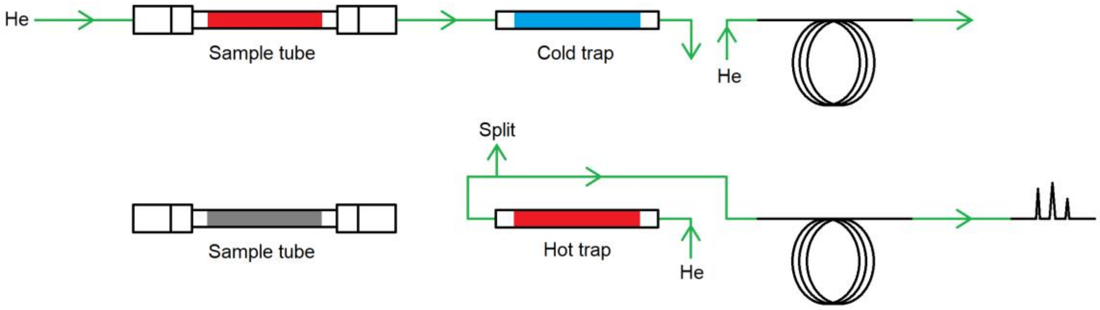


Figure 2. Scheme showing the two stages of thermal desorption, the tube desorption and the trap desorption.

Mass spectrometry[16] (MS) is a popular detector combined with gas chromatography, due to its high selectivity and sensitivity. The main components of an MS detector are the ion source, where energy is provided to ionize the analytes, and the mass analyser, where the obtained ions are separated according to their m/z ratio.

The most common types of ion source are electron ionisation (EI) and chemical ionisation (CI). The main difference between them is the type of ions obtained: with EI the molecules are bombarded with an electron beam at energies much higher than the one required for ionization of the compound, so there is fragmentation of the molecule; while with CI, which includes the use of a reagent gas, fragmentation is minor, so the molecular ion is obtained. The ion source used in this work is EI, since the fragmentation is characteristic for each molecule and that eases identification of the peaks.

The two mass analysers most used in combination with gas chromatography are quadrupoles and ion traps. Both select those ions which will pass to the detector itself by variations of voltage, but they differ in geometry: the quadrupole, as its name indicates, is formed by four poles while the ion trap is a monopole. The analyser used in this work is a quadrupole[15].

2.3. Online analysers

Automated analysers are an interesting tool for monitoring of many contaminants. In fact, there are many reference methods used by the public administrations for this purpose. The Government of Catalonia manages a network of sampling points[17] throughout the territory intended for the monitoring and forecast of atmospheric contamination, where automated methods are used for the determination of major air pollutants such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), particulate matter (PM_{10} and $PM_{2.5}$), carbon monoxide (CO), ozone (O_3), benzene (C_6H_6) and hydrogen sulfide (H_2S).

These analytes are of many types and the methods used for their determination vary widely in nature, so the focus in this case is on the method used for benzene, the VOC regulated by the

Spanish Royal Degree 102/2011 related to air quality in immission zones[18]. Its automated monitoring is done following the standard method UNE-EN 14662-3:2016[19], using automated pumped sampling with in situ gas chromatography.

The instruments used for this method are online gas chromatographs which involve multiple steps (*Figure 3*) in an automated manner, all governed by a 10-step valve which isolates the different circuits. First the sample is sucked into the instrument by generating low pressure in a cylinder, and passes through a trap to preconcentrate the analytes. This sampling is done multiple times to reach higher concentrations and to have representation of the whole sampling period. A flow of nitrogen is then passed through the trap in the opposite direction to remove any possible retained oxygen and avoid unwanted oxidation reactions of the analytes.

Finally, the analytes are thermally desorbed by heating of the trap and they are carried towards the column by the nitrogen flow. First, they pass through a stripper column, where the larger molecules which will not be analysed are retained and then removed with a backflush, and then through the analysis column. Once separated, the analytes reach the detector, in this case a photoionization one.

The whole cycle can last from 15 minutes to 1 hour, depending on the instrument, and thanks to the 10-step valve the sampling and the analysis occur simultaneously, so while an analysis is performed the instrument is already preconcentrating the sample for the next one.

The photoionization detector (PID)[20] uses electromagnetic radiation in the UV range to ionize organic compounds, especially aromatic ones, into the corresponding molecular cation and an electron (*Reaction 1*). Those cations are then neutralized in the cathode and the current required for that neutralization is directly proportional to the amount of compound, so it can be used for its quantification.

$$M + h\nu \rightarrow M^{+} + e^{-} \qquad Reaction\ 1$$

Active sampling methods, such as this one, can be used to check the results obtained by passive sampling. The advantage of these automated gas chromatographs against other active methods is that the sampling is continuous or semi-continuous, so the whole passive sampling period is well represented.

These automated or online analysers exist not only for monitoring of benzene but for other organic contaminants as well. In this work, two instruments of this type are used, one for the determination of 1,3-butadiene and the other for benzene, toluene, ethylbenzene and the three structural isomers of xylene (BTEX).

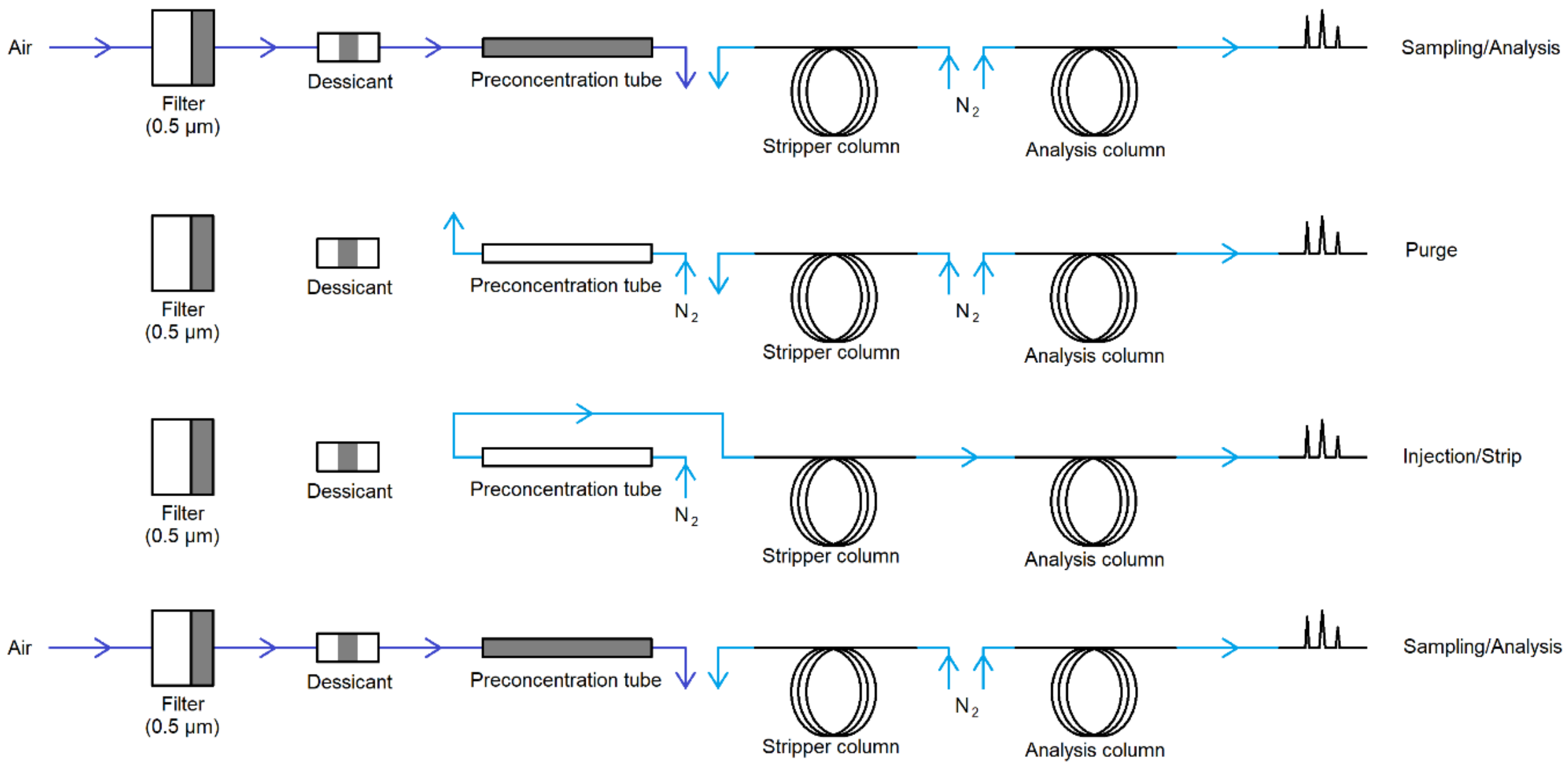


Figure 3. Scheme showing the stages of the online gas chromatograph: first the sampling and adsorption of analytes on the preconcentration tube, then the purge of that tube to remove oxygen, then the desorption of the tube and injection into the stripper column where they are separated, and finally the analysis which occurs simultaneously with the sampling.

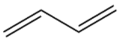
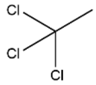
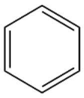
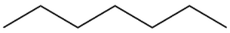
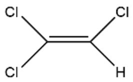
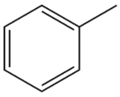
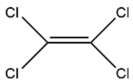
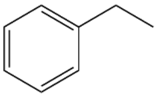
3. Experimental part

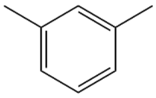
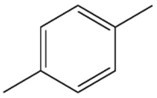
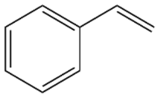
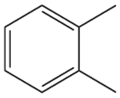
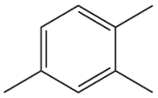
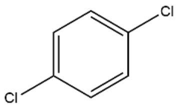
3.1. Reagents and standards

The standards of the 15 studied VOCs (*Table 1*) used for validation of the passive sampling methods include standard commercial mixture EPA 502/524 Volatiles Organic Calibration Mix of 2000 μg mL^{-1} in methanol (Supelco, Bellefonte, USA), as well as individual standards of *n*-hexane and *n*-heptane (Sigma-Aldrich, Steinheim, Germany), with purities of 99%. Stock solutions of these last two compounds were prepared in methanol with approximate concentrations of 2000 μg mL^{-1}. 1,3-butadiene standard solution of 20% weight in toluene (Sigma-Aldrich, Steinheim, Germany) was diluted to 2000 μg mL^{-1}. Working solutions of 100 μg mL^{-1} and 10 μg mL^{-1} were prepared in methanol (14 VOCs) and toluene (1,3-butadiene) and stored in the freezer at -19 ºC.

Methanol was HPLC-GOLD-Ultragradient Grade, from Carlo Erba Reagents (France), and toluene was gas chromatography grade, from J.T. Baker (Gliwice, Poland). Helium and nitrogen gases used for the chromatographic analysis, the cryogenisation of the trap and the conditioning of the adsorbent tubes were purchased with 99.999% purity from Carburos Metálicos (Tarragona, Spain).

Table 1. List of analytes.

Compound	CAS No.	Structure	MW[21] (g/mol)
1,3-Butadiene	106-99-0		54.09
n-Hexane	110-54-3		86.18
1,1,1-Trichloroethane	71-55-6		133.40
Benzene	71-43-2		78.11
n-Heptane	142-82-5		100.20
Trichloroethene	79-01-6		131.38
Toluene	108-88-3		92.14
Tetrachloroethene	127-18-4		165.80
Ethylbenzene	100-41-4		106.16

m-Xylene	108-38-3		106.16
p-Xylene	106-42-3		106.16
Styrene	100-42-5		104.15
o-Xylene	95-47-6		106.16
1,2,4-Trimethylbenzene	95-63-6		120.19
1,4-Dichlorobenzene	106-46-7		147.00

The standards used for calibration of the online GC analysers are two 1,3-butadiene bottles of 200 and 2000 ppb and a BTEX bottle of 100 ppb, all in nitrogen and from Carburos Metálicos (Tarragona, Spain). The bottle of nitrogen used as carrier gas by these analysers was also purchased from Carburos Metálicos.

3.2. Sampling tubes

There are three types of tubes used for passive sampling in this work (*Table 2*). The first two are radial tubes and the last are axial tubes. Their characteristics are presented in this section.

Table 2. Passive sampling tubes with their main characteristics.

	RADIELLO® 141	**RADIELLO® 145**	**FLM® Carbopack X**
Diffusion direction	Radial	Radial	Axial
Adsorbent	Carbopack X (graphitised carbon)	Carbograph 4 (graphitised carbon)	Carbopack X (graphitised carbon)
Sampling time	1 week	1 week	2 weeks

The Radiello® tubes used for radial passive sampling are manufactured in Padova, Italy by the Istituti Clinici Scientifici Maugeri and were purchased from Merck. The ones used for analysis of 1,3-butadiene (code RAD141) were stainless-steel mesh tubes filled with approximately 480 mg of graphitized carbon solid adsorbent Carbopack X (particle size 40/60 mesh), of 6 cm of length, 5 mm of outer diameter and 4.8 mm of inner diameter. The ones used for analysis of the other

VOCs (code RAD145) were similar tubes filled with a different type of graphitized carbon material, Carbograph 4 (particle size 35/50 mesh). For sampling, these tubes are placed inside yellow radial diffusive bodies made of a high-thickness microporous polyethylene membrane (code RAD1202) which are then mounted on support plates (code RAD121) as seen in *Figure 4*.

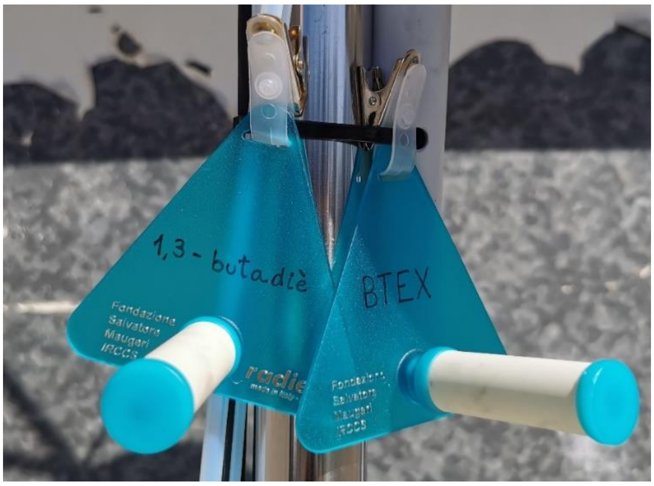


Figure 4. The two radial passive sampling tubes placed in their diffusive bodies and mounted on their support plates at the sampling point.

The tubes used for axial passive sampling were stainless-steel tubes of 9 cm of length, 6.35 mm of outer diameter and 4.5 mm of inner diameter, filled with 600 mg of Carbopack X adsorbent. They were purchased from Supelco (Bellefonte, USA). They have a sampling directionality shown by an arrow on the external surface (*Figure 5*), so the compounds enter through a diffusive cap on one of the tips and a brass stopper is placed on the other.

Figure 5. Two axial passive sampling tubes, the upper one with the two brass stoppers used to avoid contamination when not in use and the lower one with the diffusive cap on the corresponding end.

The axial passive sampling tubes are conditioned before their use by passing a flow of nitrogen (100 mL/min) during 3 hours at 330 ºC. Tube blanks are done for both types of samplers before sampling to ensure the absence of retained impurities.

3.3. Sampling

The selected sampling point is El Morell, a village of 3,803 inhabitants[22] located next to the Northern Industrial Park of Tarragona and the oil refinery, the two ethylene cracking plants and the multiple polymers production plants housed there.

Air samples from El Morell were collected (*Figure 6*) over the span of 6 months (between November 2022 and April 2023, see *Annex 1* for the exact sampling periods), to see the effect of varying meteorological conditions on the performance of the two types of passive samplers. In the Mediterranean climate, thermal inversion tends to occur during the autumn and winter months, trapping the contaminants close to the emission area and impeding their dispersion, while in the hotter spring months they should be more easily carried away by atmospheric currents. Therefore, the concentrations are expected to be higher in winter.

The used radial passive tubes have a recommended sampling time of 7 days to avoid both saturation and back diffusion[11], while the axial tubes require 14 days of sampling[15]. The average values obtained for these periods of time are then compared with those obtained by the online GC-PID analysers installed at the sampling point, for 1,3-butadiene and for BTEX.

The temperature and pressure information used for the correction of the sampling uptake rates of the passive samplers is obtained from the Government meteorological station in Constantí, about 4.5 km away from the sampling point[23].

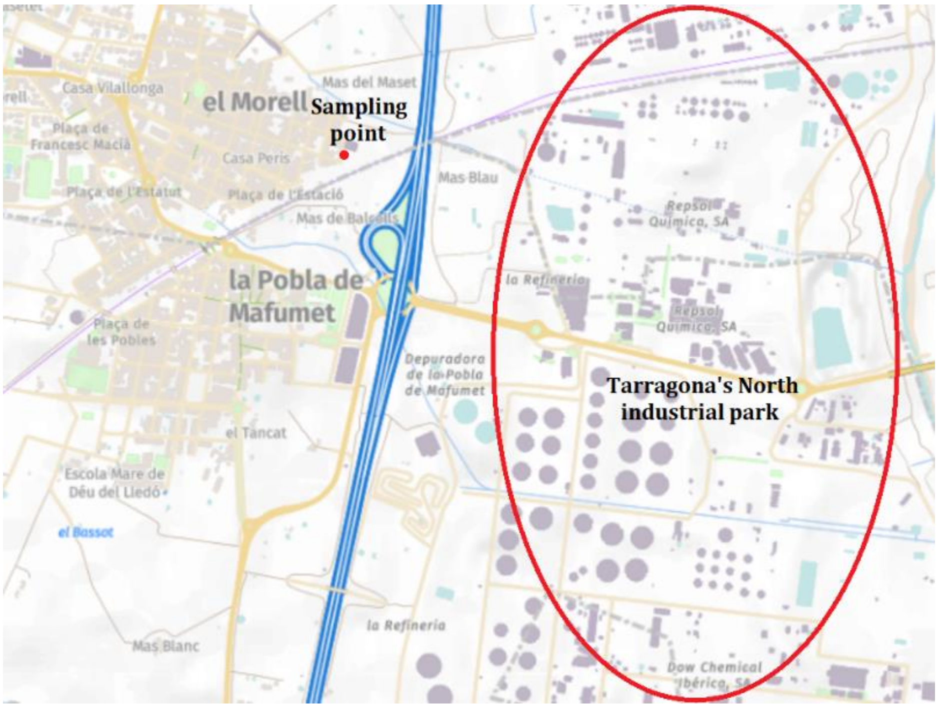


Figure 6. Map of Tarragona's North industrial park showing the sampling point in El Morell and the closest towns (El Morell and La Pobla de Mafumet).[24]

3.4. Thermal desorption and chromatographic analysis

The analytes retained in the tubes are extracted with an ULTRA-xr thermal desorption autosampler coupled to a UNITY-xr thermal desorber, both from Markes International (Cardiff, United Kingdom). The focusing trap contains graphitised carbon and was purchased from Markes International as well. The used gas chromatograph is a 7890A GC System with a ZB-5 capillary column (5% phenyl-95% dimethylpolysiloxane), coupled to a 5975C inert mass spectrometer with triple-axis detector, both from Agilent technologies (Santa Clara, California, USA).

The method and separation used in this work were previously optimized in the research group, as shown in the articles by Maceira et al.[25] and Vallecillos et al.[15]. More detailed parameters of the TD-GC-MS analysis are shown in *Table 3*.

Table 3. Parameters of the TD-GC-MS analysis.

Thermal desorption	Pre-purge	Flow	20 mL min^{-1}
		Time	1 min
		Temperature	Room temperature
		Mode	Split (5 mL min^{-1})
	Tube desorption (1st stage)	Time	10 min
		Temperature	330 ºC
		Flow	20 mL min^{-1} (Helium)
		Mode	Splitless
		Cold trap	General purpose graphitised carbon trap, -25 ºC
	Trap desorption (2nd stage)	Time	10 min
		Temperature	330 ºC
		Mode	Split (5 mL min^{-1})
		Flow path temperature	180 ºC
Chromatographic analysis	GC	Column	ZB-5 (-60ºC – 340 ºC) 60 m x 0.32 mm, 1 μm thickness
		Flow	1.2 mL min^{-1} (Helium)
		Temperature program	40 ºC for 5 min 6 ºC min^{-1} to 140 ºC 15 ºC min^{-1} to 220 ºC for 8 min

	MS	Ionization source	EI, 70 eV, 230 ºC
		Analyzer	Quadrupole, 150 ºC
		Transfer line temperature	280 ºC
		Mode	Full-scan
		m/z range	35 to 280

The analysers used for in situ online gas chromatography at the sampling point were a Synspec B. V. Alpha 403 analyser for monitoring of 1,3-butadiene and a Syntech Spectras GC 955-600 analyser for monitoring of BTEX, whose analysis parameters (shown in *Table 4*) are programmed by the provider and cannot be modified.

Table 4. Parameters of the online gas chromatographs.

Synspec B.V. α 403	Sampling	Sample strokes	10
		Tube adsorbent	Tenax-GR
		Temperature (tube desorption)	200 ºC
		Cycle time	30 min
	Separation	Oven temperature	45 ºC
		Column flow	1.5 mL min^{-1} (Nitrogen)
		Pressure	4 bar
	Detector	Ionisation voltage	-4000 mV
Syntech Spectras GC 955-600	Sampling	Sample strokes	5
		Tube adsorbent	Tenax-GR
		Temperature (tube desorption)	180 ºC
		Cycle time	15 min
	Separation	Oven temperature	50 ºC
		Column flow	1.6 mL min^{-1} (Nitrogen)
		Pressure	4 bar
	Detector	Ionisation voltage	-4000 mV

3.5. Calibration

For the quantification of the analytes of the passive sampling methods, standards of different concentrations were prepared from the stock and working solutions to build the external standard calibration curves and stored at -19 ºC.

Axial sorbent tubes were spiked with 1 μL of the corresponding standard solution using a 10 μL syringe and the sandwich technique, which involves sandwiching the desired amount of injection solution in air. To do this the tube is mounted on a calibration solution loading ring (Markes, Llantrisant, USA), and once it has been spiked it is purged for 5 min with helium to evaporate the solvent, with a flowrate of 100 mL min^{-1} for the VOCs standards in methanol and of 50 mL min^{-1} for the 1,3-butadiene standards in toluene, according to the procedure described in the UNE-EN 14662-1 norm[26].

The standard solutions were prepared to have between 0.01 and 500 ng of analytes in the tubes after injection, to fix limits of detection (LOD) and quantification (LOQ) and linear range.

On the other hand, the calibration of the online GC analysers is done using gaseous standards starting from a bottle of fixed concentration. This fixed concentration is diluted using a system for dynamic dilution MCV CAL 110 (MCV, Collbató), which mixes the standard with zero air (N_2/O_2) to obtain the desired concentration. For 1,3-butadiene two different bottles are used, because due to the proximity of the production plants some peaks are expected which could not be determined using only the bottle of low concentration (200 ppb). For BTEX, the most significant compound in the area is benzene, but since it is regulated by law high peaks are not expected. This calibration is done about once every two months to ensure that there has not been a drift in the signal of the PID lamp and that the identification window is still adequate.

4. Results and discussion

4.1. Chromatographic separation

Even when the method has already been developed such as in this case, the chromatographic separation must be checked. This is done by first doing two desorptions of one tube and ensuring that in the second desorption there are no significant amounts of analytes present, meaning that as expected everything inside the tube is desorbed during a single thermal desorption.

Then a single standard of 10 ng (or in this case two standards, one for 1,3-butadiene and the other for the rest of VOCs) is injected to make sure that all the expected compounds appear at their expected retention time. To identify the peaks, the ions and their relative abundance (*Table 5*) obtained by MS are compared with the NIST library and with the aforementioned articles from the same research group[15,25]. During their development of the method it was ensured that all the peaks were well separated.

In the case of this method, the acquisition type is full scan. This is because the method was originally developed for a wide range of compounds (108 analytes) and the windows needed to develop a method using SIM acquisition, which is programmed to detect only the ions for the specific compound which appears at a certain retention time, would be too small to obtain reliable results. Each analyte is identified by one quantifier ion, whose concentration is used as the 100% reference, and two or three qualifier ions, whose amount when compared to the quantifier ion must remain close to the ratio shown in parentheses in *Table 5*.

The chromatogram of one of the radial passive samples can be seen below (*Figure 7*). In this case the chromatogram shows the full scan of ions and the labels for each of the analysed compounds.

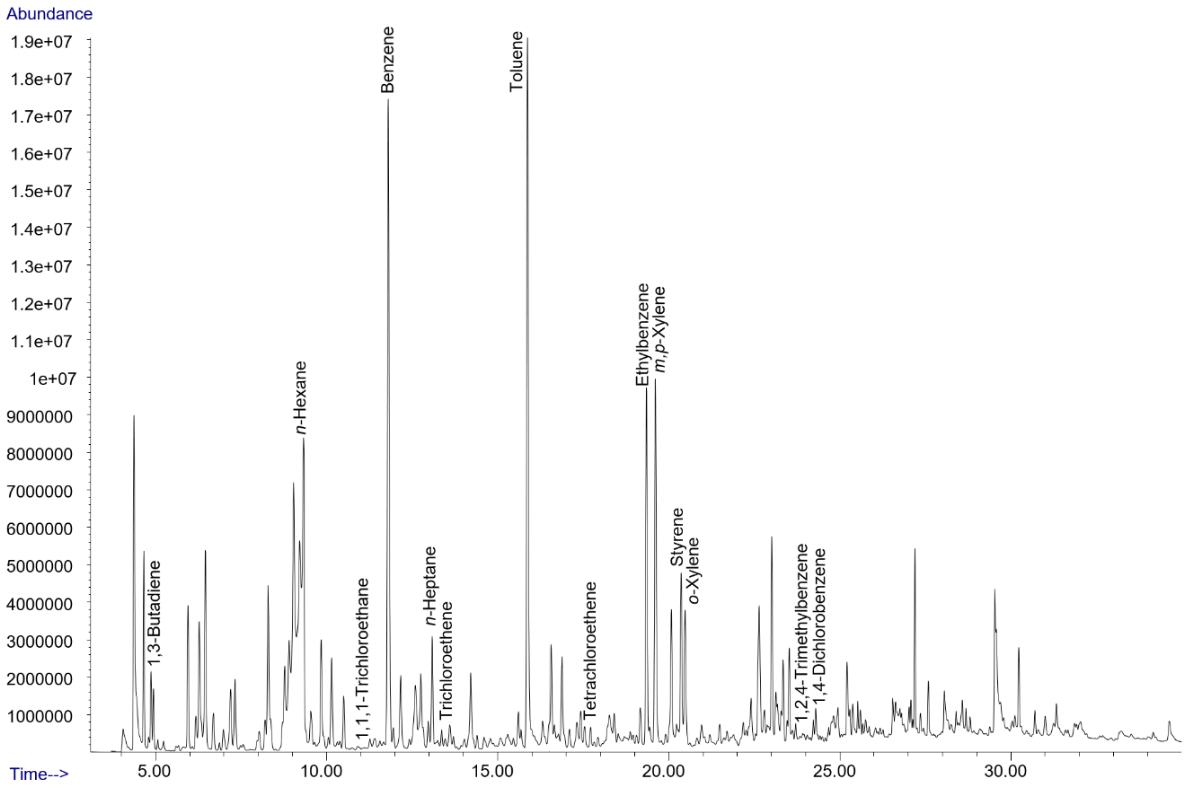


Figure 7. Example chromatogram of one of the analysed samples.

4.2. Validation

For the calibration of the passive sampling, the standards were originally injected all in different tubes which were all desorbed one after the other. This showed problems for the detection of some of the compounds at low concentrations, especially the chlorinated ones, and *n*-hexane and benzene did not seem to show a linear behaviour.

For this reason, the tubes were first conditioned with nitrogen at 330 ºC to clean it completely and then some blanks of these tubes were done. They showed a constant amount of both *n*-hexane and benzene as residue which could not be removed, so the calibration was done by calculating an average of those residues and subtracting it from the integration of the spiked tubes. This new calibration (*Table 5*) allowed reaching lower instrumental limits of detection (LOD), which are chosen as the standard with a signal of at least 3 times the base noise, and quantification (LOQ), which are the first point of the calibration curve. For *n*-hexane and benzene the LOD was chosen as the first standard which showed an integration of three times above the average of the residue.

As seen in *Table 5*, some of the analytes showed multiple linear ranges. This is especially important in a work such as this one because the two types of samplers adsorbed very different amounts of analyte due to their different geometry, so it was expected that the desorption of the axial sampling tubes would yield results in the low linear range while the radial ones would be in the high linear range. All the calibration curves showed coefficients of determination (r^2) higher than 0.9975.

Since the method of the online GC analysers comes set from the manufacturer, their separation has already been optimized and the only required validation is the calibration. The standard of each concentration is injected multiple times until its area has stabilized and then to obtain three or four repetitions of each point. Usually, the calibration curve is automatically included in the instrument so that the results are already given in ppb, which is the case of the instrument for measuring BTEX (1 to 10 ppb), but for the 1,3-butadiene analyser two linear ranges were observed, one from 1 to 15 ppb and the other from 15 to 100 ppb.

Table 5. Characteristics of the calibration of the instrumental thermal desorption method for each analyte.

Compound	t_R (min)	Quantifier ion	Qualifier ions	LOD (ng)	LOQ (ng)	Linear range
1,3-Butadiene	4.86	54	53 (69%), 50 (31%), 39 (85%)	0.1	0.2	0.2 – 15 ng 15 – 500 ng
n-Hexane	9.19	57	86 (23%), 71 (7%), 41 (60%)	0.5	5	5 – 150 ng 150 – 500 ng
1,1,1-Trichloroethane	11.2	97	119 (17%), 99 (65%), 61 (35%)	0.02	0.05	0.05 – 15 ng
Benzene	11.5	78	77 (22%), 52 (12%), 51 (13%)	0.1	0.5	0.5 – 150 ng 150 – 500 ng
n-Heptane	13.1	43	71 (65%), 57 (56%), 41 (58%)	0.05	1	1 – 150 ng
Trichloroethene	13.3	130	132 (95%), 97 (61%), 95 (93%)	0.05	0.1	0.1 – 5 ng
Toluene	15.7	91	92 (60%), 65 (9%), 63 (6%)	0.05	5	5 – 150 ng 150 – 500 ng
Tetrachloroethene	17.6	166	164 (77%), 131 (55%), 129 (54%)	0.05	0.1	0.1 – 5 ng 5 – 150 ng
Ethylbenzene	19.1	91	106 (35%), 77 (8.6%), 65 (8.8%)	0.05	1	1 – 25 ng 25 – 100 ng 100 – 400 ng
m,p-Xylene	19.4	91	106 (56%), 105 (24%), 77 (11%)	0.05	0.5	0.5 – 150 ng
Styrene	20.2	104	103 (46%), 78 (35%)	0.05	0.2	0.2 – 100 ng
o-Xylene	20.3	91	106 (53%), 105 (20%), 77 (11%)	0.05	0.5	0.5 – 150 ng
1,2,4-Trimethylbenzene	23.6	105	120 (57%), 79 (13%), 77 (20%)	0.05	0.5	0.5 – 200 ng
1,4-Dichlorobenzene	24.2	146	148 (64%), 111 (29%), 75 (26%)	0.02	0.05	0.05 – 5 ng

4.3. Data processing

4.3.1. Online GC analysers

The data obtained from the online GC analysers is in ppb in air, which is the same as m^3 of analyte per 10^9 m^3 of air. To be able to compare these results with those obtained by the other methods they must first be converted to µg of analyte per m^3 of air. This can be done by modifying the ideal gas law as shown in *Equation 3*.

$$PV = nRT \quad \rightarrow \quad \frac{n}{V} = \frac{P}{RT} \quad \rightarrow \quad \frac{m/M}{V} = \frac{P}{RT} \quad \rightarrow \quad \frac{m}{V} = \frac{PM}{RT} \tag{3}$$

And assuming a pressure of 1 atmosphere and knowing the value of R, the expression for the ratio between the mass of analyte and the ratio it occupies is (*Equation 4*):

$$\frac{m}{V} = 12187\frac{M}{T} \tag{4}$$

Which can be used as a conversion factor (*Equation 5*) to convert ppb to µg· m^{-3}:

$$\frac{x\,m^3\;analyte}{10^9\;m^3\;air} \cdot \frac{12187 \cdot \frac{M}{T}\;g\;analyte}{1\;m^3\;analyte} \cdot \frac{10^6\;\mu g\;analyte}{1\;g\;analyte} = \left(12.187 \cdot \frac{M}{T} \cdot x\right) \frac{\mu g\;analyte}{m^3\;air} \tag{5}$$

And from which the following simplified expression[27] (*Equation 6*) is obtained:

$$\mu g \cdot m^{-3} = \frac{ppb \cdot 12.187 \cdot M}{273.15 + {}^{\underline{o}}C} \tag{6}$$

where M is the molecular weight of the compound and ${}^{\underline{o}}C$ is the temperature recorded by the online analyser in Celsius degrees. Once all the data obtained from the online GC analysers has been converted to µg · m^3, the average values for the sampling periods are obtained.

The main advantage of online GC analysers against passive sampling is that the concentrations of the analytes can be monitored constantly to obtain monthly graphs such as the following ones (*Figure 8*) where one can see the magnitude and abundance of peaks. In this example, 1,3-butadiene shows some significant peaks against a homogeneous background of low concentrations, due to the closeness of the production plants and the lack of legislation for this compound in Spain and in the EU. Despite the proximity of production plants, only a few peaks of low benzene concentration have been detected, due to the strict control to which it is subjected.

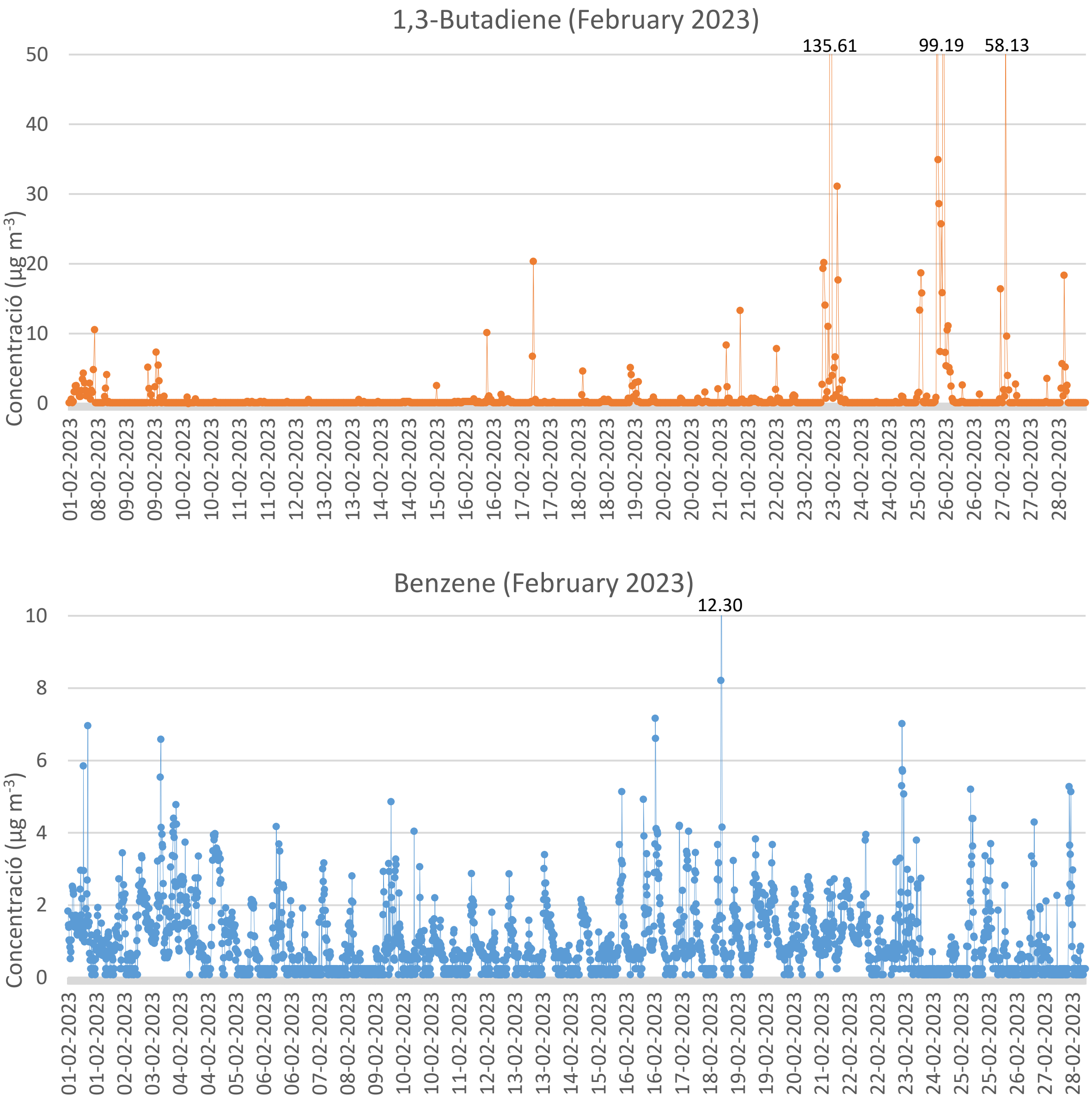


Figure 8. Concentration of 1,3-butadiene and benzene against time during the month of February of 2023.

4.3.2. Passive sampling

The passive sampling tubes were desorbed after each sampling period and then compared with the corresponding calibration curves. The result obtained is the ng present in the tube, and that must then be converted to concentration in air using equation 1 from section 2.1. To use this equation, the sampling uptake rate must first be corrected. This is done following the validation guideline for air sampling methods provided by OSHA[28] (*Equation 7*).

$$U_{exp} = U_{ref} \cdot \left(\frac{T_{exp}}{T_{ref}}\right)^{1.5} \cdot \frac{P_{ref}}{P_{exp}} \tag{7}$$

Where U_{exp} is the uptake rate in the experimental conditions, U_{ref} is the uptake rate in the reference conditions, T_{exp} is the experimental temperature, T_{ref} is the reference temperature, P_{exp} is the experimental pressure and P_{ref} is the reference pressure.

The uptake rates for radial passive sampling were extracted from the manual of the RAD145 samplers, where they are given for normal conditions of temperature and pressure (298 K and 1 atm), except for the one of 1,3-butadiene which was the experimentally determined one in the article by Strandberg et al.[11] and whose reference temperature was 295 K (and assuming a pressure of 1 atm).

The uptake rates for axial passive sampling were the experimentally determined ones in the article by Vallecillos et al.[15], at their experimental conditions of temperature and pressure, except for the three marked ones which were provided by the supplier of the tubes and were given for normal conditions of temperature and pressure.

In *Table 6* are provided the limits of detection and quantification and the upper limit of the linear range for both passive sampling methods, calculated based on the conditions for which the shown uptake rates were given in the literature and assuming a sampling period of exactly 1 week for radial sampling and 2 weeks for axial sampling.

Table 6. Calibration and uptake rates of the method.

Compound	Radial sampling				Axial sampling			
	LDM ($ng \cdot m^{-3}$)	LQM ($ng \cdot m^{-3}$)	Upper limit ($ng \cdot m^{-3}$)	U ($mL \cdot min^{-1}$)	LDM ($ng \cdot m^{-3}$)	LQM ($ng \cdot m^{-3}$)	Upper limit ($ng \cdot m^{-3}$)	U ($mL \cdot min^{-1}$)
1,3-Butadiene	2.11	4.22	10600	4.9	9.73	19.5	48600	0.51
n-Hexane	1.95	19.5	1950	25.5	40.7	407	40700	0.61
1,1,1-Trichloroethane	0.10	0.25	74.4	20.0	1.95	4.86	1460	0.51
Benzene	0.36	1.78	1780	27.8	7.09	35.4	35400	0.70
n-Heptane	0.20	3.92	588	25.3	4.07	81.3	12200	0.61
Trichloroethene	0.18	0.37	18.3	27.1	4.96	9.92	496	0.50
Toluene	0.17	16.5	1650	30.0	4.28	428	42800	0.58
Tetrachloroethene	0.20	0.39	586	25.4	4.96	9.92	14900	0.50
Ethylbenzene	0.19	1.93	1540	25.7	4.96	49.6	39700	0.50
m,p-Xylene	0.19	1.86	559	26.6	5.91	59.1	17700	0.42
Styrene	0.18	0.73	366	27.1	5.28	21.1	10600	0.47
o-Xylene	0.20	2.02	605	24.6	5.51	55.1	16500	0.45
1,2,4-Trimethylbenzene	0.23	2.26	906	21.9	5.06	50.6	20200	0.49
1,4-Dichlorobenzene	0.09	0.23	22.5	22.0	2.20	5.51	551	0.45

4.4. Method comparison

The following tables (*Tables 7 to 19*) show the results obtained for each analyte, according to sampling period and method. To compare the methods, the ratio between them is calculated. For the five analytes determined by the online GC analysers the three methods can be compared, while for the other analytes that can only be done for the two types of passive sampling. The only exception is trichloroethene, which was not found in any of the axial passive samples and therefore will finally not be included in the current study. It must be noted that the concentration of some of the analytes is very low, close to the MQL, which means that when comparing methods a ratio significantly different from 1 is obtained, but that difference can be due to errors rather than a lack of correlation between methods.

It must be noted that there was a problem with the desorption of the second axial tube and therefore that sample period will not be represented by this method. On March 18th both online GC analysers failed and could not be restarted, so they had to be sent to be repaired by the provider, which means that from that point on there is no information from them. In fact, during that reparation a leak was detected in the 1,3-butadiene analyser, which means that the data obtained through that instrument might not be completely reliable.

Table 7. Results for 1,3-Butadiene.

Compound	Sampling period	Concentration ($\mu g\ m^{-3}$)			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
1,3-Butadiene	A+B	0.38	2.66	1.38	6.98	3.61	1.93
	C+D	1.34	1.52	-	1.13	-	-
	E+F	1.85	11.61*	6.48	6.27	3.50	1.79
	G+H	0.66	4.01	1.32	6.10	2.00	3.05
	I+J	2.12	5.27	4.47	2.48	2.10	1.18
	K+L	-	1.71	2.63	-	-	0.65
	M+N	-	1.98	3.14	-	-	0.63
	O+P	-	10.76*	8.65	-	-	1.24

* These results were an average of integrations higher than the upper limit of the linear range and obtained by extrapolation.

The average concentrations of 1,3-butadiene obtained by the three methods vary widely. In general, those obtained by passive sampling are much higher than those obtained by the online GC analyser, which can be due to the aforementioned leak in the analyser. At the same time, those obtained specifically by radial passive sampling are much higher than those obtained by axial passive sampling, specially during the coldest months.

Table 8. Results for *n*-Hexane

Compound	Sampling period	Concentration (μg m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
n-Hexane	A+B	0.73	-	-
	C+D	0.18	-	-
	E+F	1.91	0.84	2.26
	G+H	0.69	1.04	0.67
	I+J	0.51	3.20	0.16
	K+L	0.48	0.58	0.83
	M+N	0.37	0.43	0.85
	O+P	0.59	0.75	0.78

The average concentrations obtained for *n*-hexane are all below 2 μg m^{-3} except for the fifth value of axial sampling. The first period of axial sampling showed a very high value (above 16 μg m^{-3}) which could only be due to a contamination of the used tube for this analyte, so it was removed from the results. The ratios between the radial and the axial sampling methods tend to be lower than 1, and that means that in this case the concentrations obtained through radial tubes could be an underestimation.

Table 9. Results for 1,1,1-Trichloroethane

Compound	Sampling period	Concentration (ng m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
1,1,1-trichloroethane	A+B	3.23	< LOQ	-
	C+D	1.81	-	-
	E+F	5.02	11.27	0.45
	G+H	4.08	10.56	0.39
	I+J	3.98	< LOQ	-
	K+L	2.36	9.88	0.24
	M+N	1.57	5.51	0.28
	O+P	1.81	7.62	0.24

In almost all cases the concentration of 1,1,1-trichloroethane obtained through axial passive sampling is significantly higher than the one obtained through radial passive sampling. The only exceptions are the two sampling periods during which the analyte was not detected in the axial tubes. In general, these concentrations are low and expressed in ng m^{-3}, so three magnitudes lower than those of other analytes and quite close to the quantification limits for the axial method, which means that even if the ratios are different from 1 the two methods could be comparable.

Table 10. Results for Benzene

Compound	Sampling period	Concentration (μg m^{-3})			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
Benzene	A+B	0.87	0.93	1.09	1.08	1.26	0.85
	C+D	1.19	0.66	-	0.55	-	-
	E+F	0.98	1.98*	1.49	2.03	1.52	1.34
	G+H	1.03	1.91*	1.29	1.86	1.25	1.48
	I+J	1.01	1.91	1.61	1.88	1.59	1.18
	K+L	-	1.59*	1.06	-	-	1.50
	M+N	-	1.10	0.92	-	-	1.20
	O+P	-	0.84	0.57	-	-	1.48

* These results were an average of integrations higher than the upper limit of the linear range and obtained by extrapolation.

Benzene seems to show a trend of behaviour for all methods. The results obtained by online GC tend to be the lowest of all, followed by the ones obtained from axial sampling. The ratio between these two methods tends to be slightly higher than one, which means that axial sampling could be quite reliable for determination of benzene. On the other hand, radial tubes seem to overestimate its concentration in most cases, obtaining results significantly higher than the online GC analyser but quite similar with the axial tubes. The average value of the concentration of benzene for all methods is below the permitted 5 μg m^{-3} annual average[3,18] in immision zones.

Table 11. Results for *n*-Heptane

Compound	Sampling period	Concentration (μg m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
n-Heptane	A+B	0.26	< LOD	-
	C+D	0.23	-	-
	E+F	0.31	0.17	1.85
	G+H	0.42	0.10	4.02
	I+J	0.24	0.16	1.46
	K+L	0.20	0.06	3.23
	M+N	0.18	0.10	1.82
	O+P	0.20	0.07	2.99

The results obtained for *n*-heptane through both methods of passive sampling show quite low concentrations, but due to the small values any small variation between the two makes the ratio differ significantly from 1. There is a trend for concentration determined by radial tubes to be higher than the one determined by axial tubes.

Table 12. Results for Toluene

Compound	Sampling period	Concentration ($\mu g\ m^{-3}$)			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
Toluene	A+B	2.33	1.46	1.03	0.63	0.44	1.42
	C+D	3.44	1.26	-	0.37	-	-
	E+F	1.80	1.69*	1.37	0.94	0.76	1.24
	G+H	2.65	2.12*	1.45	0.80	0.55	1.46
	I+J	1.92	1.78*	1.39	0.93	0.72	1.28
	K+L	-	1.20	0.79	-	-	1.52
	M+N	-	1.00*	0.76	-	-	1.33
	O+P	-	1.12	0.74	-	-	1.51

* These results were an average of integrations higher than the upper limit of the linear range and obtained by extrapolation.

For all sampling periods the concentration of toluene determined through passive sampling is lower than the one obtained by the online GC analyser, which means that for this analyte both types of passive sampling underestimate the average concentration, with radial sampling being the one that yields results closest to the ones of online GC. The concentrations of toluene are slightly higher than those obtained for other analytes, but that is because the sampling site is a municipal warehouse, and the compound might have been released by the materials stored there.

Table 13. Results for Tetrachloroethene

Compound	Sampling period	Concentration ($\mu g\ m^{-3}$)		C_{radial}/C_{axial}
		Radial	Axial	
Tetrachloroethene	A+B	0.07	0.08	0.95
	C+D	0.03	-	-
	E+F	0.05	0.04	1.23
	G+H	0.28	0.17	1.65
	I+J	0.04	0.04	1.04
	K+L	0.06	0.05	1.21
	M+N	0.05	0.04	1.23
	O+P	0.03	0.03	1.18

The behaviour for both types of passive sampling for tetrachloroethene seems to be very similar since the ratio between the two groups of results is close to 1 for all sampling periods and even at low concentrations. According to these results, the concentration of this analyte in the area always remains quite low.

Table 14. Results for Ethylbenzene

Compound	Sampling period	Concentration ($\mu g\ m^{-3}$)			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
Ethylbenzene	A+B	0.25	0.52	0.45	2.08	1.78	1.17
	C+D	0.24	0.32	-	1.31	-	-
	E+F	0.42	0.96	2.68	2.26	6.33	0.36
	G+H	0.17	0.64	0.58	3.78	3.44	1.10
	I+J	0.22	0.63	1.74	2.90	8.04	0.36
	K+L	-	0.75	1.41	-	-	0.53
	M+N	-	0.54	1.24	-	-	0.43
	O+P	-	0.89	1.57	-	-	0.56

For ethylbenzene, the results obtained by passive sampling are always higher than those obtained by online GC. Other than that, they do not follow any specific trend, since sometimes the results obtained with radial sampling are higher than those obtained with axial sampling and other times it is the other way around. In general, the determined concentrations of ethylbenzene always remain below 2 $\mu g\ m^{-3}$.

Table 15. Results for *m,p*-Xylene

Compound	Sampling period	Concentration ($\mu g\ m^{-3}$)			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
m,p-Xylene	A+B	0.72	0.23	0.15	0.32	0.20	1.57
	C+D	1.04	0.20	-	0.19	-	-
	E+F	0.63	0.33	0.61	0.52	0.97	0.54
	G+H	0.73	0.41	0.18	0.57	0.25	2.31
	I+J	0.57	0.37	0.46	0.66	0.80	0.82
	K+L	-	0.24	0.20	-	-	1.18
	M+N	-	0.21	0.17	-	-	1.23
	O+P	-	0.35	0.30	-	-	1.17

Both types of passive sampling tend to underestimate the concentration of *m,p*-xylene when compared to online GC, but there is no trend in the underestimation remaining constant for either type of passive sampling. Their relation is also not constant, since the ratio between the two kinds of tubes varies a lot through the different sampling periods. In general, the determined concentrations of *m,p*-xylene always remain below 1 $\mu g\ m^{-3}$, so the change in ratios might be due to the low concentrations rather than actual discrepancies between methods.

Table 16. Results for Styrene

Compound	Sampling period	Concentration (μg m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
Styrene	A+B	0.10	< LOD	-
	C+D	0.09	-	-
	E+F	0.29	0.23	1.30
	G+H	0.14	< LOQ	-
	I+J	0.15	0.04	3.54
	K+L	0.14	0.02	6.71
	M+N	0.08	0.05	1.67
	O+P	0.15	0.05	3.31

The concentrations obtained for styrene through radial sampling are always higher than those obtained through axial sampling, but the ratio between the two varies all through the sampling periods so this difference between sampling methods does not remain constant. The concentrations determined through both methods always remain below 0.3 μg m^{-3}.

Table 17. Results for *o*-Xylene

Compound	Sampling period	Concentration (μg m^{-3})			C_{radial}/C_{GC}	C_{axial}/C_{GC}	C_{radial}/C_{axial}
		Online GC	Radial	Axial			
o-Xylene	A+B	0.31	0.16	0.19	0.53	0.63	0.85
	C+D	0.54	0.16	-	0.29	-	-
	E+F	0.43	0.26	0.46	0.60	1.06	0.56
	G+H	0.30	0.29	0.17	0.98	0.57	1.72
	I+J	0.32	0.24	0.29	0.75	0.89	0.84
	K+L	-	0.16	0.16	-	-	1.04
	M+N	-	0.14	0.13	-	-	1.04
	O+P	-	0.22	0.21	-	-	1.07

Similarly to what happens with the other two isomers of xylene, passive sampling methods tend to underestimate the concentration of *o*-xylene when compared to online GC, but there is no trend in the underestimation remaining constant for either type of passive sampling. Their relation is also not constant, since the ratio between the two kinds of tubes varies a lot through the different sampling periods. In general, the determined concentrations of *m,p*-xylene always remain below 0.5 μg m^{-3} so, like for *m,p*-xylene, the change in ratios might be due to the low concentrations rather than actual discrepancies between methods.

Table 18. Results for 1,2,4-Trimethylbenzene

Compound	Sampling period	Concentration (µg m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
1,2,4-Trimethylbenzene	A+B	0.07	< LOD	-
	C+D	0.05	-	-
	E+F	0.26	1.72	0.15
	G+H	0.18	1.07	0.17
	I+J	0.14	1.32	0.10
	K+L	0.10	1.14	0.09
	M+N	0.09	0.66	0.14
	O+P	0.08	0.95	0.08

The average concentrations obtained for 1,2,4-trimethylbenzene with the radial tubes are all below 0.3 µg m^{-3} while for the axial tubes they are slightly higher but below 2 µg m^{-3}. The ratios between the radial and the axial sampling methods are always significantly lower than 1, and that means that the concentrations obtained through radial tubes could be an underestimation.

Table 19. Results for 1,4-Dichlorobenzene

Compound	Sampling period	Concentration (ng m^{-3})		C_{radial}/C_{axial}
		Radial	Axial	
1,1,1-trichloroethane	A+B	3.23	< LOQ	-
	C+D	1.81	-	-
	E+F	5.02	11.27	0.45
	G+H	4.08	10.56	0.39
	I+J	3.98	< LOQ	-
	K+L	2.36	9.88	0.24
	M+N	1.57	5.51	0.28
	O+P	1.81	7.62	0.24

The results obtained for 1,4-dichlorobenzene with both passive sampling methods are low, with concentrations similar to those detected for 1,1,1-trichloroethane. This means that even if the ratios between the radial and the axial sampling methods are always significantly lower than 1, this could be because the concentrations are close to the MLQ.

To summarize for all the compounds, as seen by the ratios obtained the results vary widely when using the different techniques and for the different analytes. The only ones that behave somewhat as expected are the three isomers of xylene, for which the concentrations determined through online GC are slightly higher than those from the passive methods (*Figure 9*). For the other four analytes represented in these online GC analysers the results are quite different, since the passive samplers overestimate the concentration (*Figure 9*). The ratio when comparing the results of benzene from the axial tubes and from the online GC system is usually close to 1, but it is the only compound for which that occurs.

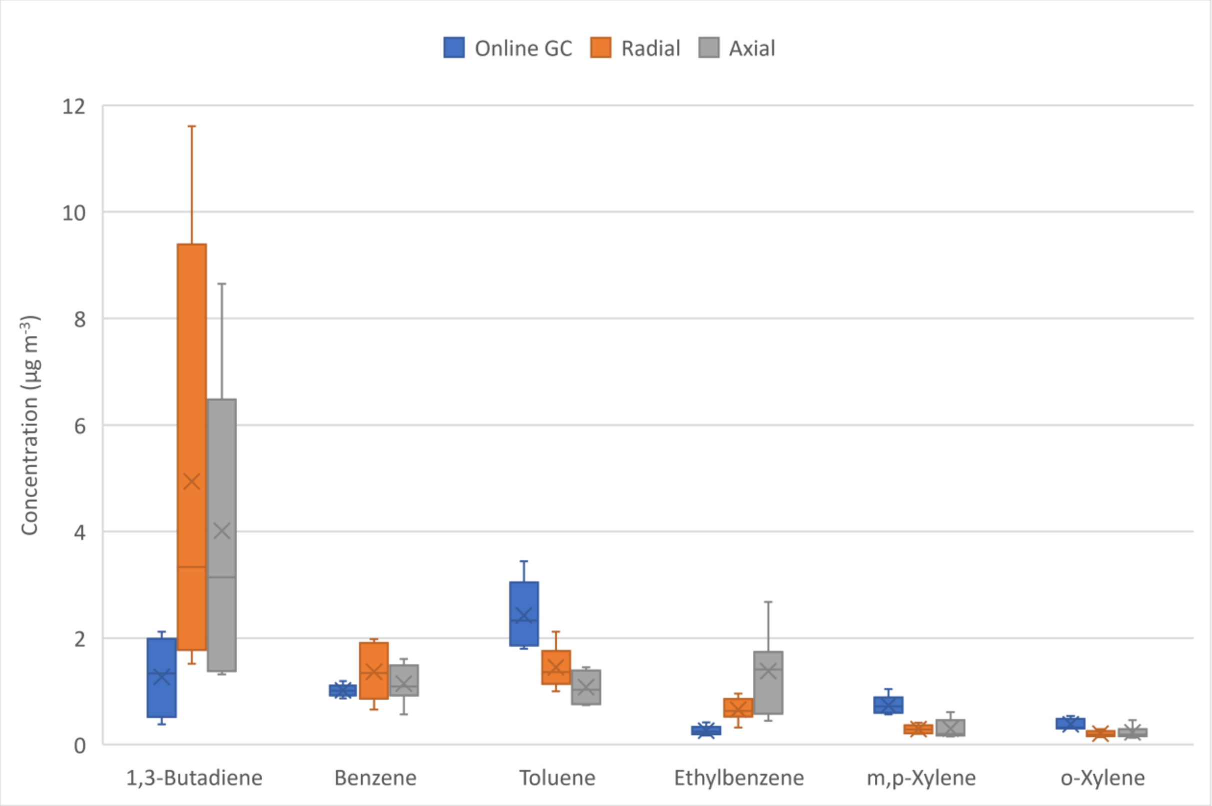


Figure 8. Box and whisker chart with the concentrations of the six analytes which are determined with the three methods.

In the diagram above, 1,3-butadiene shows a high difference between the three methods, with the concentration obtained by the online analyser being much lower and with a much lower dispersity. The use of online GC analysers for determination of 1,3-butadiene has already been compared to the use of axial passive sampling in the same research group[29,30], and in those cases there were no significant differences between methods. But during the duration of the current study there was a leak in the analyser, so the difference in concentrations might be due to that rather than an inadequate performance of the passive samplers.

When looking at the compounds which were only analysed with passive methods, there are no trends apart from the fact that for most of them the concentrations determined with radial tubes are lower than those determined with axial tubes, but there is no regular relationship between the two so it seems that either could be affected by external conditions.

5. Conclusions

The obtained results showed that passive sampling is not a reliable or representative technique in these specific conditions. This is probably due to the presence of many variations in the concentrations of the analytes during the sampling period, since some of them are seen to have quite high and sharp peaks in the data obtained from the online GC analysers. These episodes are not well-represented by passive sampling of either kind because the short period during which the analytes are present in air might not allow for their complete diffusion into the adsorbing material, which is what might have happened for the xylenes. On the other hand, if those peaks appear at the end of the sampling period a high amount of analyte might be retained in the passive samplers leading to an overestimation of the concentrations, which is what might have happened for the other four compounds analysed by online GC.

The only compound for which there seems to be some agreement between online GC and axial passive sampling, and a significant difference with radial passive sampling, is benzene, which is the only compound of the list regulated by law, and therefore, as seen in *Figure 8*, its industrial emissions are quite controlled and if there are any peaks they are not high enough to distort much the concentrations. The three isomers of xylene also followed one of the expected trends, since the concentrations obtained by passive sampling were always lower than those obtained by the online GC analyser, and since their concentration is quite low the difference in ratios can be explained by uncertainty of the methods.

For this reason, and especially for those compounds which are most toxic (benzene, 1,3-butadiene and trichloroethylene), and in places where their presence is most expected due to industrial activities, a good monitoring with online GC analysers is required.

To further verify the reliability of passive sampling methods, they should be studied in environments where the sources of pollution are more uniform, such as urban areas. There, the results obtained with axial passive samplers are expected to be more in accordance with those obtained by continuous sampling with online GC, since the average value will be obtained from a more regular distribution of concentrations and the only changing variable will actually be the environmental conditions.

Nevertheless, the evaluation of their performance in more "extreme" environments such as the one in this work should be continued to obtain more information, since it is true that the scope of this study was limited due to problems with the instrumentation and there is no information from online GC during part of the sampling period.

Conclusions

Els resultats obtinguts mostren que el mostreig passiu no és fiable o representatiu en aquestes condicions específiques. Això seria causat per la presència de grans variacions en les concentracions dels anàlits durant el període de mostreig, ja que alguns d'ells presenten puntes bastant altes i estretes en les dades obtingudes amb els analitzadors en línia. Aquests episodis no són ben representats pel mostreig passiu de cap dels dos tipus perquè el període curt en què els anàlits són presents a l'aire pot no permetre la seva difusió completa al material adsorbent, que és el que hauria passat amb els xilens. Per altra banda, si aquests pics apareixen cap al final del període de mostreig els mostrejadors passius podrien retenir una alta quantitat d'anàlit, portant a una sobreestimació de les concentracions, que és el que podria haver passat amb els altres quatre compostos analitzats per GC en línia.

L'únic compost pel qual sembla que hi ha certa concordança entre el GC en línia i el mostreig passiu axial, i una diferència significativa amb el mostreig passiu radial, és el benzè, que és l'únic compost de la llista regulat per llei i, per tant, com es pot veure en la *Figura 8*, les seves emissions industrials són bastant controlades i si hi ha algun pic no és prou alt per distorsionar les concentracions. Els tres isòmers de xilè també segueixen una de les tendències predites, ja que les concentracions obtingudes per mostreig passiu sempre són més baixes que les obtingudes per l'analitzador de GC en línia, i com que la seva concentració és bastant baixa la diferència dels quocients es podria explicar per la incertesa dels mètodes.

Per aquesta raó, i especialment pels compostos més tòxics (benzè, 1,3-butadiè i tricloroetilè), i en aquells llocs on la seva presència és esperada per les activitats industrials, és recomanable un bon monitoratge amb analitzadors GC en línia.

Per verificar la fiabilitat dels mètodes de mostreig passiu caldria estudiar-los en ambients on les fonts de contaminació són més uniformes, com en àrees urbanes. Allí s'espera que els resultats obtinguts amb mostrejadors passius axials estiguin més en concordança amb els obtinguts per mostreig continu amb GC en línia, ja que la mitjana obtinguda seria fruit d'una distribució més regular de concentracions i les úniques variables canviants serien realment les condicions ambientals.

Tanmateix, l'avaluació del seu funcionament en ambients més "extrems" com el d'aquest treball s'hauria de continuar per obtenir-ne més informació, ja que és cert que l'abast d'aquest estudi està limitat per problemes amb els instruments i no hi ha informació dels equips en línia durant part del període de mostreig.

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Annexes

Annex 1. Sampling periods with meteorological characteristics

	Weekly sampling period	Time (min)	Mean T (ºC)	Mean P (hPa)	Biweekly sampling period	Time (min)	Mean T (ºC)	Mean P (hPa)
A	23/11/2022 – 30/11/2022	10080	13.0	1018.6	23/11/2022 – 07/12/2022	20160	10.5	1016.5
B	30/11/2022 – 07/12/2022	10080	8.8	1014.4				
C	07/12/2022 – 14/12/2022	10080	10.6	1005.7	07/12/2022 – 21/12/2022	20160	11.2	1011.4
D	14/12/2022 – 21/12/2022	10080	12.2	1015.9				
E	11/01/2023 – 18/01/2023	10080	9.6	1015.5	11/01/2023 – 25/01/2023	20160	7.9	1017.3
F	18/01/2023 – 25/01/2023	10080	6.2	1017.3				
G	09/02/2023 – 16/02/2023	10410	6.7	1034.1	09/02/2023 – 23/02/2023	20490	8.3	1029.3
H	16/02/2023 – 23/02/2023	10080	9.7	1024.7				
I	23/02/2023 – 02/03/2023	10050	7.1	1010.8	23/02/2023 – 08/03/2023	18480	8.4	1012.0
J	02/03/2023 – 08/03/2023	8430	9.5	1014.0				
K	08/03/2023 – 15/03/2023	10080	16.5	1013.9	08/03/2023 – 23/03/2023	21600	14.6	1015.7
L	15/03/2023 – 23/03/2023	11520	12.6	1017.6				
M	23/03/2023 – 30/03/2023	9930	14.1	1019.9	23/03/2023 – 13/04/2023	30210	14.2	1018.2
N	30/03/2023 – 13/04/2023	20280	14.2	1017.4				
O	13/04/2023 – 21/04/2023	11730	14.8	1013.7	13/04/2023 – 27/04/2023	20490	15.6	1014.1
P	21/04/2023 – 27/04/2023	8760	15.7	1013.9				